

SECOND LAW ANALYSIS, FOR PINPOINTING THE TRUE INEFFICIENCIES IN FUEL CONVERSION SYSTEMS

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Introduction

Presented in this paper is the methodology for fundamental thermodynamic analysis of energy conversion systems. Examples are taken from representative coal gasification unit operations, to illustrate the method in the context of synfuel systems. Such analyses accurately pinpoint and evaluate the dissipations in a plant, as well as the efficiency of each device. Being a "second law" analysis, it is based on the concept called availability,* in contrast to the usual "first law" analysis which uses only the energy concept.

The results are not simply of academic interest; they are of real practical value in many ways, as the article discusses. Many engineering, administrative, executive and political decisions are made under the impressions -- misimpressions -- given by energy analyses. In a recent article, former Chief Engineer C. A. Berg (1) of the FPC stressed the necessity to apply availability analyses in lieu of energy analyses, in order to measure rationally the effectiveness with which fuels and resources are put to use; among other things, he points out examples of mismanagement resulting from the above-mentioned misimpressions. The Federal Energy Administration has recently supported several studies based on the second law (13,14); one of these studies, by physicists from Princeton and Michigan, was reported recently, in Science (22).

For some time prominent thermodynamicists (e.g. 5, 6, 15, 16, 17, 18) have proposed the more extensive use of availability analyses. One reason they have not been taken up enthusiastically is because the concept of availability itself has seemed abstract and difficult to understand, as a result of complex derivations, from obtuse statements of the second law. The causes of the complexity are historical -- quirks in the way thermodynamics evolved. But very significant progress has been made lately and thermodynamics, including availability, can now be presented in a very palatable manner, while making its practical importance and value much clearer.

The results of second law analyses are much more enlightening than first law (energy) analyses, because the dissipations and efficiencies measured with availability are the true ones, whereas those measured with energy are erroneous and misleading. What the scientist calls "energy" is not the resource society values. What the layman calls "energy" is that resource, but the layman's "energy" is synonymous with "availability."

When does the layman ascribe "energy" to a material? When it has a potential to cause change for him. But that which is called energy by the scientist is not this potential; our energy cannot be produced or destroyed. Therefore, if it were truly a resource it would be nondepletable. We cannot resolve this paradox by saying that "it is conserved, but it is degradable." Because, if energy loses

*Other words have been used as alternatives to "availability"; e.g., available energy, available work, useful energy, exergy, essergy and others -- including "potential energy", which will be used synonymously in this article.

potential to cause change for us then energy cannot be a measure of that potential. The only true resolution of the paradox is to realize that it is availability -- potential energy -- which is the rational measure of potential to cause change for us.

It is potential energy that is needed to make processes go; in so doing, it is literally used up -- not degraded, not converted, but used up (consumed).

"Energy converters", such as engines, take potential energy in one form and convert it, in part, to another form; the part which is not converted is used up to accomplish the conversion. We could say that the consumed portion "fuels" the conversion process.

The following article is broken down into (1) a summary of the fundamentals of thermodynamics, (2) a description of how these are applied, especially for the availability analysis of synfuel operations, (3) the results of the analysis of some coal gasification unit operations, and (4) the summary and conclusions, including a survey of results for other systems and economic sectors.

Thermodynamics -- Its Basic Implications

The basic concepts of Thermodynamics are the two commodities called Energy and, here, Potential Energy.^{*} The basic principles are the First Law, dealing with energy, and the Second Law, dealing with potential energy.

To illustrate the basic concepts and principles, consider Figure 1, showing a conduit carrying some commodity. It could portray a transmission line through which electric charge is flowing with a current I_q (e.g., amperes = coulombs per second). Or, it might be a penstock carrying volumes V of high-pressure water at a current I_v (such as gpm = gallons per minute), perhaps headed for a hydraulic turbine. The conduit could be a pipeline carrying amounts n of a chemical such as H_2 at a current I_{H_2} (such as gram-moles/second). Or it could be a heat conductor carrying a thermal current I_θ . The conduit could be carrying any commodity.

Whatever the commodity might be, energy is carried concurrently with it. For examples, past any "station" along a transmission line, such as past the cross-section depicted in Figure 1, the rate P_E at which energy E flows past is proportional to the rate I at which the commodity flows past. If the commodity is charge, then we can write that the energy current -- the "power" -- is $P_E = \phi I_q$ where ϕ is the value of the electric potential at the "station." $P_E = \phi I_q$ can be called the rate of electric flow of energy, associated with the electric current I_q .

When a virtually incompressible fluid carries energy solely by virtue of being pressurized, there is a hydraulic flow of energy at the rate $P_E = p I_v$, where p is the pressure and I_v is the volumetric flow rate. When a material flows and carries energy not only because of its pressure but also because of its composition, the flow of energy can be called a chemical flow; e.g., if H_2 is flowing with a current I_{H_2} moles per second, $P_E = \mu_{H_2} I_{H_2}$ where μ_{H_2} is the chemical potential.

Notice that, in each of the above examples, the proportionality factor between the commodity current and the associated energy current (energy power flow) turns

^{*}The commodity that we call potential energy, here, has gone by a variety of names, such as availability. The traditional "potential energy" -- that of a mass in a gravitational field, at an altitude above some reference datum ("ground") -- is one form of potential energy.

out to be the "potential" which drives the commodity current through the conduit. Stated more precisely, a difference in the potential, from one end of the conduit to another, causes the current to flow through the conduit.

Whatever the commodity is that is flowing -- and several may be flowing simultaneously -- there is a flow of energy associated with the flow of each commodity, and hence for each commodity there is a proportionality coefficient (like p or ϕ or v_{H_2}) relating the associated energy current (i.e., power) P_E to the commodity current I .

The driving force which causes the thermal current is temperature difference; and, $P_E = TI_\theta$. Traditionally, in science and engineering, it is P_E which has been called the rate of heat flow. It would have been better to use the word "heat" for the commodity with current I_θ , but this commodity was not recognized until later; it is entropy.

Commodity Balances, and the First Law

In analysis of energy converters balances are applied -- implicitly, if not explicitly -- to the different converters for each of the relevant commodities; for examples, mass balances, energy balances, chemical compound balances, entropy balances, and so on. The amount of any given commodity in some container can in general be changed by either (1) transporting the commodity into or out of the container, or (2) production or consumption inside. Thus, on a rate basis {The rate of change in the amount of the commodity contained} = {The sum of all of the inlet rates} - {The sum of all of the outlet rates} + {The rate of production inside} - {The rate of consumption inside}. For the special case of steady operation, the amount of any content is constant, so that the rate of change of the content is zero. Then, the totals of the rates of influx and the productions equals the totals of the effluent rates plus consumptions.

Some commodities, like charge, cannot be produced or consumed; they are said to be conserved. The essence of the First Law is, of course, that energy is conserved; there is another aspect: the transport of any commodity has an associated energy transport, as illustrated by the foregoing discussions of currents in conduits.

The Potential to Cause Change for us: a Commodity

When does a commodity have the capacity to cause changes for us? The answer is: whenever it is not in complete, stable equilibrium with our environment. Then, it can be used to accomplish any kind of change we want, to some degree. Thus, charge has this capacity whenever it is at a potential different from "ground"; water has this capacity whenever it is at a pressure different from "ground."

Water in a tower has capacity to cause change for us; we could use it to cause any kind of change for us, to some degree. For example, we could use it to take charge -- of some limited amount -- out of the "ground" and put it on a given capacitor. Once the capacitor has been charged, the charge is now at a potential above "ground." Thus, it now has some of the capacity to cause change for us given up by the water. If we liked, we could use the capacity now residing in the capacitor to pump water back into the tower. But certainly no more water than was used to charge the capacitor. How close could we come to getting all that water back up? Clearly that depends on (1) how efficiently we did the task of transferring the water's original capacity to the charge -- on what fraction of the original capacity was ultimately transferred to the charge and on what fraction was consumed to accomplish that transfer, and in turn, (2) how efficiently we transfer the charge's capacity back to the water. Practically, whatever the desired transformation is, some capacity to cause change must be consumed by the equipment which accomplishes the transformation; capacity to cause change ("fuel")

must be used up to make the transformation proceed.

Capital is needed to improve the efficiency of our transformations. Given boundless capital (for equipment and time) that we could invest for use in charging the capacitor by lowering the water, and then for pumping it back by discharging the capacitor, we could come as close as we would like to returning the original amount of water to the tower, but never more. That is the theoretical limit.

Figure 2 depicts equipment for accomplishing the transfer of "capacity to cause change" from the charged capacitor to the water. As the charge flows from the capacitor through the motor its potential drops to the "ground" value -- the equilibrium value, in our environment. The decrease in potential is given up to torque in the drive shaft which in turn transmits it via the pump to the water, taken from the reservoir. The pump increases the potential of the water, its pressure, from "ground" pressure (atmospheric) to that pressure corresponding to the water tower head.

At an instant when current is flowing from the capacitor at potential ϕ , and through the motor at a rate I_q , then the theoretical limit on the water flow rate I_v is given by $I_v]_{\text{maximum}} = [\phi - \phi_0]I_q / [p - p_0]$ where ϕ_0 is ground potential, p_0 is "ground" (i.e., atmospheric) pressure at the pump inlet and p is the pressure at the pump outlet. The relationship for I_v follows from the fact that the rate of hydraulic energy increase of the water $[p - p_0]I_v$ cannot exceed the rate of electric energy decrease of the charge $[\phi - \phi_0]I_q$. The greater $[p - p_0]$, the smaller can the maximum I_v be. Whether a small amount of water is having its potential increased greatly or a large amount is having its potential increased slightly, the maximum "capacity to cause change", $[p - p_0]I_v$, that the water will be acquiring would be the same. The maximum $[p - p_0]I_v$ would equal the "capacity to cause change" being given up by the charge, $[\phi - \phi_0]I_q$, which is the "potential energy" decrease of the charge -- the energy decrease associated with bringing it to complete equilibrium with our environment (to "ground"). Under these ideal conditions, the potential energy (or availability) flowing out $P_{A,\text{out}} = [p - p_0]I_v$ equals the potential energy (availability) flowing in $P_{A,\text{in}} = [\phi - \phi_0]I_q$.

Such ideal operation is the theoretical limit which can be approached but never reached in practice. Associated with real motors and pumps, there will always be dissipations of potential energy -- consumption thereof -- used up to make the motor and pump "go." These dissipations manifest themselves in "heat production"; if steady operating conditions are to be maintained -- which we will assume, here, since it will help illustrate certain important points -- the "heat" (entropy) which is produced must be transferred away, eventually flowing into our atmosphere at "ground" temperature, T_0 . The thermal current into the atmosphere, I_θ , will need to equal the rate of "heat" (entropy) production in this steady case, and the associated energy transfer will be $T_0 I_\theta$. The energy balance for the composite, saying energy efflux equals energy influx, now yields $\phi I_q + p_0 I_v = \phi_0 I_q + p I_v + T_0 I_\theta$. Hence, $[p - p_0]I_v = [\phi - \phi_0]I_q - T_0 I_\theta$. That is, the potential energy output will be less than the input by the amount consumed to "drive" the transformation:

$$P_{A,\text{out}} = P_{A,\text{in}} - \dot{A}_c$$

where $\dot{A}_C = T_0 I_\theta$ represents the rate of availability consumption -- rate of potential energy consumption.

Effectiveness -- The True Efficiency

In the theoretical limit, potential energy supplied with any commodity can be completely transferred to any other commodity. In the case of real transformations, the degree to which this perfection is approached is measured by the so-called effectiveness (4, 16, 17):

$$\epsilon = \frac{\text{potential energy in product}}{\text{potential energy supplied}}$$

For the composite of motor and pump just considered, the true measure of how well the "capacity to cause change" was converted from the electrical to hydraulic form is given by

$$\epsilon = \frac{[p - p_0]I_V}{[\phi - \phi_0]I_q} = \frac{P_{A,out}}{P_{A,in}}$$

The denominator exceeds the numerator by the amount of potential energy consumed, $\dot{A}_{consumed}$: $\epsilon = [P_{A,out}] / [P_{A,out} + \dot{A}_C]$. For any conversion, the theoretical upper limit of ϵ is 100 per cent, which corresponds to the ideal case with no dissipations. To approach that limit, in practice, requires greater and greater capital investment of money and/or time. The tradeoff, then, is the classical one: operating costs (for fuel) versus capital (for equipment and time). An important point here is that optimization of this tradeoff can be greatly facilitated by the application of Second Law analyses, applying potential energy analyses to processes, devices and systems (5, 6, 7, 10, 11, 17, 18, 19).

Conventional efficiencies and unit product costs defined in terms of "product" energy and "fuel" energy are generally faulty, to a degree which depends upon the kind of device or system to which they are applied. Basically, their worth is proportional to how well they approximate the effectiveness, ϵ .

Thermal and Chemical Potential Energy

Recall the relationship $\dot{A}_C = T_0 I_\theta$ for the special circumstances illustrated in Figure 2. Since I_θ equals the rate of entropy production, \dot{S}_p , the special equation $\dot{A}_C = T_0 I_\theta$ illustrates the general relationship $\dot{A}_C = T_0 \dot{S}_p$, which says that the rate of "heat" (entropy) production is proportional to the rate of potential energy consumption. It must be emphasized that $T_0 I_\theta$ does not represent potential energy "escaping to the environment" in Figure 2, but potential energy consumed within the composite of motor, pump, etc.; it does represent energy flowing into the environment, but it has no capacity to cause change since it is at "ground" temperature T_0 -- at equilibrium with our environment.

In actuality, the temperature of the system components rises as a result of the dissipations inside. Therefore the thermal current leaving from the surface σ would not be at T_0 but at a higher temperature T_σ , carrying potential energy at a rate $[T_\sigma - T_0]I_\theta$. Thus, a small amount of potential energy does escape thermally -- a small fraction of the energy escaping thermally.

Whenever we have a thermal current I_θ at a temperature $T_\sigma \neq T_0$, we could use a "heat cycle" (thermal motor) whose work output could be used say to drive a generator. In the theoretical limit with no dissipations inside the cycle or generator, the electric output would be $P_{A,elec} = [\phi - \phi_0]I_q = [T_\sigma - T_0]I_\theta$. Since

the energy input to the cycle is $P_{E, \text{thermal}} = T_0 I_\theta$ we can rewrite the latter as $P_{A, \text{elec}} = [1 - (T_0/T_\theta)] P_{E, \text{thermal}}$; or $W = [1 - (T_{\text{out}}/T_{\text{in}})] Q$, which is the classic result, usually derived in a complex manner from obtuse "Second Law" statements.

With algebraic combination of an energy balance and a potential energy balance on the composite of Figure 2 for this case with $T_\theta > T_0$ we would again find $\dot{A}_c = T_0 \dot{S}_p$ -- a general relationship.

When charge flows at a rate I_q , $P_E = \phi I_q$ and $P_A = [\phi - \phi_0] I_q$. When entropy flows at a rate I_θ , $P_E = T I_\theta$ and $P_A = [T - T_0] I_\theta$. When a chemical j diffuses at a rate I_j , $P_E = \mu_j I_j$ and $P_A = [\mu_j - \mu_{j0}] I_j$, where μ_{j0} is the chemical potential of j in the reference environment. When there is bulk flow of a material, carrying entropy too, $P_E = \mu_j I_j + T I_\theta = [\mu_j + T s_j] I_j = h_j I_j$ and $P_A = [\mu_j - \mu_{j0}] I_j + [T - T_0] s_j I_j = [h_j - T_0 s_j - \mu_{j0}] I_j$.

The Second Law

Potential energy does represent the capacity to cause change for us. It is a commodity. It is distinct from energy; it is not the same commodity. Energy cannot serve as a measure of capacity to cause change for us; only potential energy (availability) can. Some might be inclined to claim the contrary, arguing that the distinction is artificial, since the difference between an energy flow like ϕI_q with charge (or $p I_v$ for "incompressible fluids") and the corresponding potential energy flow $[\phi - \phi_0] I_q$ is a trivial difference which can be eliminated by measuring the potential relative to ground. Thus, if $\phi_0 \equiv 0$ then $\phi = [\phi - \phi_0]$. As a matter of fact, for commodities such as charge (and volume of "incompressible fluids"), which are conserved, the "ground" potential can be arbitrarily set to zero, with no disruptions. But for other, non-conserved commodities "ground" potential cannot be set to zero; for example, "ground" temperature T_0 cannot be arbitrarily defined to be zero.

In summary, then, energy does not in general represent the "capacity to cause change for us"; energy flows associated with non-conserved commodities are not representative of such capacity. And, energy associated with such commodities cannot, even in the ideal limit, be completely transferred to other commodities.

Potential energy, which anything has when it is not in complete equilibrium with our environment, does represent the capacity to cause change for us. It can be transferred from one thing to any other (but completely only in the ideal limit). In actuality, to accomplish changes for us some potential energy is invariably used up, because it is needed to make the changes occur. This paragraph presents the essence of the Second Law.

Energy is not the commodity we value; potential energy (availability) is.

The Methodology of Availability Analyses

To improve the operating "fuel" economy of an "energy" system means to lessen the potential energy consumed within the system and that lost in effluents so that, for a specified amount of product, the amount of potential energy -- "fuel" -- that needs to be supplied is thereby decreased. The overall effectiveness of the system is a measure of the prospects for improvement of fuel economy. The lower the effectiveness, the greater the prospects.

To ascertain the consumption losses and effectiveness requires the evaluation of the rates at which availability (potential energy) is transferred in and out with different commodities. These calculations involve exactly the same type of

procedures as the evaluation of energy flows.

Not only is an overall analysis of an "energy" system valuable, but so is a detailed analysis which pinpoints where and to what extent the availability consumptions occur, within the system. The procedures for making a more detailed analysis are identical to those for the overall analysis. It is simply a matter of applying balances to subsystems of the overall system. In turn, components can be broken down and analyzed further, process by process.

Application to Coal Gasification Systems

In this paper the methodology of availability analysis will be illustrated by application to the Koppers-Totsek gasification system, illustrated in Figure 3 and in Table 1; the tabular data are taken directly, calculated or estimated from Farnsworth et al (8, 9).

Consider the combination of coal preparation and gasifier units. An availability balance says that the rate at which availability enters equals that at which it leaves plus the rate of consumption

$$A_1 + A_2 + A_3 + A_6 + A_7 + A_8 + A_{25} + A_{26} = A_{10} + A_4 + A_9 + A_c$$

The only useful product is A_{10} , therefore the effectiveness of this system is

$$\epsilon = \frac{A_{10}}{A_1 + A_3 + A_6 + A_7 + A_{25} + A_{26}}$$

where the combustion air, free from the environment, has zero availability ($A_2 = 0$) and the water, free except for purification, has very little ($A_8 \approx 0$). The difference between the numerator and denominator consists of A_c , the availability consumed to drive the processes, plus $A_4 + A_9$ which are waste losses to the environment.

The gas leaving at 10 is an ideal gas mixture with composition shown in Table 1. The availability transferred per mole flowing is

$$a_{10} = h_{10} - T_0 s_{10} - \sum x_{j10} \mu_{j0} = \sum x_{j10} [h_j(T_{10}) - T_0 s_j(T_{10}, x_{j10} p_{10}) - \mu_{j0}]$$

The evaluation of these quantities, by standard thermodynamic property calculations, are shown in the Appendix, along with a handy tabulation of formulas for evaluating the terms for each constituent. The results, for the flow streams referred to above, give

$$A_{10} = m_{10} a_{10} = 1.8247 \frac{\text{kg}}{\text{kg coal}} \cdot 12387 \frac{\text{kJ}}{\text{kg}} = 22602 \frac{\text{kJ}}{\text{kg coal}}$$

$$A_3 = 1582 \frac{\text{kJ}}{\text{kg coal}}$$

$$A_6 = 123.8 \frac{\text{kJ}}{\text{kg coal}}$$

$$A_7 = 39.25 \frac{\text{kJ}}{\text{kg coal}}$$

$$4.184 \frac{\text{kJ}}{\text{kg}} = 1 \frac{\text{kcal}}{\text{kg}} = 1.8 \frac{\text{Btu}}{\text{lb}}$$

The electrical transport rates are given directly by the estimated values of

$$A_{25} = 15.2 \frac{\text{kJ}}{\text{kg coal}}$$

$$A_{26} = 73.6 \frac{\text{kJ}}{\text{kg coal}}$$

The availability of the coal described in Table 1 turns out to be

$$a_{\text{coal}} = 11710 \frac{\text{Btu}}{\text{lb coal}}$$

Substitution of all these quantities into the expression yields

$$\epsilon_{\text{system 1}} = \frac{22602}{29052} = 0.78$$

The combination of consumption and losses is equal to the sum of the inputs minus the output of product:

$$A_c + A_{\text{losses}}]_{\text{system 1}} = A_c + A_4 + A_8 = 29054 - 22602 = 6453 \frac{\text{kJ}}{\text{kg coal}}$$

This consists primarily of availability consumption, for driving the processes. The loss with flue gases and hot slag are

$$A_4 = 104.2 \frac{\text{kJ}}{\text{kg coal}} \quad A_9]_{\text{hot}} = 580 \frac{\text{kJ}}{\text{kg coal}}$$

This leaves, for the total consumption by processes within the system,

$$A_c = 5769 \frac{\text{kJ}}{\text{kg coal}}$$

If the hot slag is merely quenched, essentially to atmospheric temperature, and no use is made of A_9 , then the 580 kJ/(kg coal) is consumed by the quenching process.

A similar analysis has been made on the combination of oxygen-production unit, steam-generation unit, and clean-up unit. It was found that

$$A_c]_{\text{system 2}} = 2452 \frac{\text{kJ}}{\text{kg coal}}$$

with losses of

$$A_{16} = 899.6 \frac{\text{kJ}}{\text{kg coal}} \quad A_{14} = 69.9 \frac{\text{kJ}}{\text{kg coal}}$$

and outputs of

$$A_{17} = 17485 \frac{\text{kJ}}{\text{kg coal}} = 4179 \frac{\text{kcal}}{\text{kg coal}} = 7522 \frac{\text{Btu}}{\text{lb coal}}$$

$$A_{18} = 715 \frac{\text{kJ}}{\text{kg coal}} \quad A_3 = 1582 \frac{\text{kJ}}{\text{kg coal}}$$

$$A_6 = 123.8 \frac{\text{kJ}}{\text{kg coal}} \quad A_7 = 39.25 \frac{\text{kJ}}{\text{kg coal}}$$

Thus, the effectiveness with which system 2 would operate, with the supposed data employed here, is

$$\epsilon_{\text{system 2}} = \frac{\Sigma A_{\text{out}}}{\Sigma A_{\text{in}}} = \frac{\Sigma A_{\text{out}}}{\Sigma A_{\text{out}} + \Sigma A_{\text{loss}} + A_c} = \frac{19945}{19945 + 970 + 2452} = 0.85$$

The power plant illustrated in Figure 3 is taken to be a conventional power plant, with the exception that it utilizes the export steam, stream 18 from heat recovery. (Of course, that steam could be used for a variety of alternate purposes, instead.) As shown by Gaggioli et al (1975), the effectiveness with which the power plant uses A_{17} is $\epsilon \sim 0.4$, while it uses A_{18} with $\epsilon \sim 0.8$. Therefore, the total electricity production by the power plant is

$$A_{\text{elec}} = 0.4 A_{17} + 0.8 A_{18} = 7566 \frac{\text{kJ}}{\text{kg coal}}$$

The net electricity production by the whole system, A_{27} , is this 7566 kJ/(kg coal) less that used in-plant:

$$A_{27} = 7566 - 132 - 3 - 9 - 15 - 74 = 7333 \frac{\text{kJ}}{\text{kg coal}}$$

The overall system effectiveness is

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$$\epsilon_{\text{overall}} = A_{27}/A_1 = 0.27$$

compared to $\epsilon \sim 0.39$ for a power plant burning relatively low-sulfur coal (Gaggioli et al, 1975).

The effectiveness of the overall gasification system per se is best gauged by

$$\epsilon_{\text{gasification}} = \epsilon_{\text{overall}}/\epsilon_{\text{power plant}} = 0.68$$

The foregoing analysis of the conversion of coal to electricity only breaks the overall system down into three major parts. By the same methods, each of these parts can be broken down further to determine the consumptions (and losses) associated (i) with each of its components, and in turn (ii) with each process in a component. Figure 4 presents such results. The results for the power plant are discussed and presented in more detail by Gaggioli et al (1975); in the appendix to that paper, the details of the availability calculations are presented for a variety of devices and processes.

Conclusions

What kinds of conclusions can be drawn from the results presented here? Some conclusions can be drawn dealing with K-T gasification per se, and some in conjunction with the power plant. For examples, where in the gasification system are there significant prospects for improvement, if anywhere? How might improvements be accomplished? Also, comparisons between the K-T and other gasification systems can be made more objectively, as well as the comparison of the relative desirability of high-Btu gasification versus low- or medium-Btu.

Consider first the K-T gasification system, itself. It is evident from the results summarized in Figure 4 that the largest dissipations are in the gasifier, due especially to the uncontrolled kinetics of reaction. The drying process, with its burning of clean product gas, is highly consumptive. There are fairly sizeable consumptions in the heat transfer from hot products, at a high $[1 - (T_0/T)]$ to jacket steam with a relatively low $[1 - (T_0/T)]$, and losses in the slag from the gasifier and in the sulfur from cleanup, as well as several other consumptions of the same order of magnitude.

Of course, no cost effective opportunities to reduce any consumption or loss should be overlooked. However, the first place to look, for striving to improve the system, is in the places where the relatively large consumptions (and losses) occur. That is probably where the better opportunities are. For the case at hand, can the chemical reactions be accomplished with less dissipation? Can they be avoided in some cases such as in drying? Can heat transfer be improved? In the end, of course, the addition of other or larger equipment for accomplishing such improvements must be cost effective. It might be that there is no hope for improvements like these; the dissipations might be inherent to the basic processes of the K-T system. If so--although the authors would not jump to that conclusion--then the analysis may be saying to look toward alternative types of systems, for gasification and/or for clean production of power from coal. (And availability analyses of the alternatives would be very worthwhile.)

Some additional remarks regarding the gasifier may be helpful to the comprehen-

*If methods could be found for economically reducing the dissipations associated with reactions on the gasifier, the same methods might be applicable to the boiler combustion--the largest single dissipation in the overall power system.

sion of the potential energy (availability) concept and its usefulness. [In the following, what may appear to be criticisms of Farnsworth et al (8, 9) are not intended to be that at all. The references to that article are incidental; numerous others could be used alternatively, though not as conveniently. The intent is not criticism, but the better appreciation of the importance of availability analyses.] Farnsworth et al claim that the overall "thermal efficiency" of system 1, basically the gasifier, is 85 to 90 per cent--that is, the "useable heat output in gas and steam divided by the total heat input to the gasifier" is 85 to 90 per cent. To cite such efficiencies--energy ratios--is misleading. The "useful energy" of the steam, its potential energy, is much less than its energy, hence energy efficiencies are generally misleading. The proper measure of how well the gasifier performs its function is the 78 per cent effectiveness. Farnsworth et al could argue that they cover this point when they say, "The cold gas efficiency, that is, the ratio of the calorific value of the gas to the calorific value of the coal, is in the range of 75 to 77 per cent." In a sense, that statement does cover the point. However, (i) it is fortuitous, inasmuch as the availability and energy of the coal are close in value, at T_0 , p_0 , and so are those of the product gas. As mentioned earlier, only in such instances is an "energy efficiency" a worthy approximation of the true efficiency; effectiveness. (For example, the true efficiency of a comfort heating furnace is less than 15 per cent, even if its "energy efficiency" were 80 per cent.) Secondly, (ii) even though today the predominant use of gas and coal is to produce heat via combustion, it is misleading to imply that the value of these commodities lie in their "calorific value". The value is in the availability (potential energy). For example if at some time in the future gas were to be used, predominantly, for the direct production of electricity, say with cells, then it would be evident that the value of the gas is not its calorific value but its availability--which represents the maximum amount of useful electricity which could be gotten from the gas, under ideal conditions. If, in turn, that electricity were used to drive a heat pump, the amount of heat deliverable is dictated by the availability of the original gas. That is, whatever transitions might occur between the gas and the heat ultimately delivered, the availability of the heat cannot exceed the availability of the gas, from which it is derived; the maximum amount of heat that could be obtained is $Q = A/[1 - (T_0/T)]$, where T is the temperature at which the heat is delivered.

If $T = 90^\circ\text{F} = 550^\circ\text{R}$, a typical value for home heating, and if outdoor temperature $T_0 = 40^\circ\text{F} = 500^\circ\text{R}$, then a cell with $\epsilon = 0.5$ in conjunction with a heat pump of today's technology, $\epsilon = 0.35$, would yield $Q = 1.93 A_{\text{gas}} = (1.93)(\text{calorific value})$.

In fact, even with today's typical power plant with $\epsilon = 0.35$, $Q = 1.35 A_{\text{gas}}$! The point, here, is not to argue in favor of heat pumps; they have many shortcomings not mentioned here, especially as T_0 drops. The point is that it is potential energy, not energy or "calorific value" which measures a commodity's usefulness for effecting changes.

Availability analyses like those presented here can be applied grossly, to overall sectors of the economy such as the industrial, the residential and commercial, and the transportation sectors to assess opportunities for improvement. These sectors can be analyzed in more detail by applying the analyses to sub-sectors, such as iron and steel, petroleum refining, aluminum and other industrial sub-sectors. In turn, each sub-sector can be analyzed in more detail by considering their different conversion systems, and so on.

All of this should be done, to determine where the potential for improvement lies. This work has begun (Reistad, 1974; Gyftopoulos et al, 1975; Hall, 1975); see Table III for a summary of typical results. The following points are noteworthy: The 10 to 15 per cent effectiveness with which energy is utilized in this country, though improved greatly over the 2 or so per cent of a century ago, is very low; basically, this is encouraging inasmuch as it shows that there is great opportunity

for improvement remaining. Conservation (in conversion, not in end-use) can contribute effectively to the resolution of the energy problem--even over the relatively short term, with today's technology--provided of course that capital is brought to bear.

Another important point which can be concluded from Figure 4 and Table III is that the production of electricity is one of our most efficient energy conversions. The great losses commonly ascribed to the stack gases and cooling water are hardly losses at all; the actual losses are elsewhere in the plant, and as a fraction of input are small compared to most conversion systems. Furnaces and all-fossil total energy systems, considered to be very efficient, are very inefficient or fairly efficient, respectively. For example, these comments have considerable negative impact on the desirability of high-Btu coal gasification and of the "Hydrogen Economy" for the purpose of distributing these synthetic fuels about for combustion in furnaces and boilers.

The foregoing methods for analyzing "energy" systems are aimed at pinpointing the losses and measuring their magnitudes and resultant per cent inefficiencies, in order to determine where opportunities for improvement and conservation lie, for the purposes of decision-making for allocation of resources-- capital, R&D effort, and so on. The methods, which involve exactly the same kinds of calculations as energy analyses, also enhance the germination of prospective ideas and the quick evaluation thereof.

Availability analyses are valuable not only for pinpointing losses but also for direct application to the design of energy systems and for other engineering projects (system modifications, maintenance, etc.), as well as for cost allocation. The key to these applications, in their infancy, (5, 6, 7, 10, 11, 18, 19, 23) is that monetary value can be assigned to the availability at the different junctures between components of a system, where availability flows from one component into another, for which it is the "fuel". Because it is availability, not energy, which "fuels" each device in a system, the only rational way of assigning monetary value (cost) to the "fuel" for each device or process is to assign the value to availability. Then for each component a rational comparison of fuel cost with other operating and capital costs can be made, for making the economically optimal selection.

APPENDIX

Details of Thermostatic Property Calculations and Tabulation of Convenient Formulas

Consider the availability transported per mole of a flowing gaseous mixture:

$$a = h - T_0 s - \sum x_j \mu_{j0}$$

where μ_{j0} is the chemical potential of species j in the reference environment.

If the mixture behaves ideally,

$$a_{\text{mix}}(T, p) = h_{\text{mix}}(T, p) - T_0 s_{\text{mix}}(T, p) - h_{\text{mix}}(T_0, p_0) + T_0 s_{\text{mix}}(T_0, p_0) \\ + \sum x_j [h_j(T_0, x_j p_0) - T_0 s_j(T_0, x_j p_0) - \mu_{j0}]$$

where h_j and s_j are the partial molar enthalpy and entropy of species j . Then

$$a_{\text{mix}}(T, p) = \int_{T_0}^T \sum_j [x_j c_{pj} - \frac{T_0}{T} c_{pj}] dT - RT_0 \ln \frac{p}{p_0} \\ + \sum_j [h_j(T_0) - T_0 s_j(T_0, x_j p_0) - \mu_{j0}]$$

And we may write

$$a_{\text{mix}}(T, p) = \sum_j a_j = \sum_j [a_{j, \text{thermal}} + a_{j, \text{pressure}} + a_{j, \text{chemical}}]$$

where

$$a_{j, t} = \int_{T_0}^T [1 - \frac{T_0}{T}] c_{pj} dT \quad a_{j, p} = RT_0 \ln \frac{p}{p_0}$$

$$a_{j, c} = h_j(T_0) - T_0 s_j(T_0, x_j p_0) - \mu_{j0}$$

If species j actually exists as a pure condensed phase in the stable reference environment, then μ_{j0} simply equals $g_j(T_0, p_0)$. If j exists as a gas in the reference environment, $\mu_{j0} = h_j(T_0) - T_0 s_j(T_0, x_{j0} p_0)$, and

$$a_{j, c} = -T_0 [s_j(T_0, x_j p_0) - s_j(T_0, x_{j0} p_0)] = RT_0 \ln(x_j/x_{j0})$$

If species j does not exist in the stable equilibrium reference environment, $a_{j, c}$ must be determined by reacting j with environmental constituents to produce other environmental constituents - in other words, by bringing j to stable equilibrium with the environment via reactions with environmental constituents. It is the chemical potentials of these products, weighted stoichiometrically, which gives μ_{j0} . Consider CO , for example. It is not stable in the atmosphere, but can react with O_2 from the atmosphere to produce stable CO_2 . Then

$$a_{\text{CO}, c} = h_{\text{CO}}(T_0) - T_0 s_{\text{CO}}(T_0, x_{\text{CO}} p_0) - \mu_{\text{CO}, 0} = g_{\text{CO}}(T_0, x_{\text{CO}} p_0) - \mu_{\text{CO}, 0}$$

$$= g_{\text{CO}}(T_0, x_{\text{CO}} p_0) + \frac{1}{2} \mu_{\text{O}_2}(T_0, x_{\text{O}_2, 0} p_0) - \mu_{\text{CO}_2}(T_0, x_{\text{CO}_2, 0} p_0)$$

$$a_{\text{CO}, c} = g_{\text{CO}}(T_0, x_{\text{CO}} p_0) + \frac{1}{2} g_{\text{O}_2}(T_0, x_{\text{O}_2, 0} p_0) - g_{\text{CO}_2}(T_0, x_{\text{CO}_2, 0} p_0)$$

The evaluation of the quantities on the right-hand side may be accomplished as follows, employing Gibbs free energy of formation and $dg|_T = v dp$.

$$g_{\text{CO}}(T_0, x_{\text{CO}} p_0) = g_{\text{CO}}(T_0, p^\circ) + [g_{\text{CO}}(T_0, x_{\text{CO}} p_0) - g_{\text{CO}}(T_0, p^\circ)]$$

Since CO behaves as an ideal gas at T_0 , between $p = x_{\text{CO}} p_0$ and p° , as long as $x_{\text{CO}} p_0$ is moderate $\Delta g = \int dg = \int v dp = \int [RT/p] dp = RT \ln(x_{\text{CO}} p_0/p^\circ)$. Thus, the foregoing equation gives

$$g_{\text{CO}}(T_0, x_{\text{CO}} p_0) = g_{\text{CO}}(T_0, p^\circ) + RT \ln(x_{\text{CO}} p_0/p^\circ)$$

Similar analyses for the O_2 and CO_2 yield

$$g_{\text{CO}_2}(T_0, x_{\text{CO}_2} p_0) = g_{\text{CO}_2}(T_0, p^\circ) + RT \ln(x_{\text{CO}_2, 0} p_0/p^\circ)$$

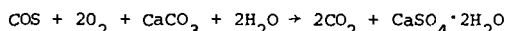
$$g_{\text{O}_2}(T_0, x_{\text{O}_2, 0} p_0) = g_{\text{O}_2}(T_0, p^\circ) + RT \ln(x_{\text{O}_2, 0} p_0/p^\circ)$$

With these three expressions, the last equation for $a_{\text{CO},c}$, for the case where $T_0 = T^\circ$ and $p = p_0 = p^\circ$, can be rewritten as

$$a_{\text{CO},c} = [g_{f,\text{CO}}^\circ + \frac{1}{2} g_{f,\text{O}_2}^\circ - g_{f,\text{CO}_2}^\circ] + RT \ln [x_{\text{CO}} (x_{\text{O}_2,0})^{1/2} / x_{\text{CO}_2,0}]$$

The first combination of terms, which can be evaluated with standard tabular values of Gibbs free energy of formation, can be called the reactive availability of the CO, while the second, logarithmic term can be called compositional availability.

Consider another case of a species j , this time for a case where one or more of the completely stable products of reaction exists as a pure condensed phase and/or one or more of the environmental constituents with which j reacts in order to reach complete stability is a pure condensed phase. As an example, suppose j is COS. It is assumed that the stable configuration of S in the reference environment is in gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; the reason for this assumption will be explained below. To get the S into this compound requires a source of Ca from the reference environment - a "free" source. That is taken to be limestone, CaCO_3 . Thus, the reaction for bringing the COS to complete, stable equilibrium with the reference environment, employing constituents from the environment alone, is



It is implicit to the foregoing that the potential for driving this reaction resides in the COS - that among the reactants and products only the COS is not in stable equilibrium with the reference environment. The net potential energy output from this reaction, under ideal conditions, is thus attributed to the COS and represents its chemical availability:

$$a_{\text{COS}}]_c = g_{\text{COS}}(T_0, x_{\text{COS}} p_0) + 2g_{\text{O}_2}(T_0, x_{\text{O}_2,0} p_0) + g_{\text{CaCO}_3}(T_0, p_0) \\ + 2g_{\text{H}_2\text{O}}(T_0, p_0) - 2g_{\text{CO}_2}(T_0, x_{\text{CO}_2,0} p_0) - g_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}(T_0, p_0)$$

Then, with manipulations like those used above for the CO,

$$a_{\text{COS},c} = [g_{f,\text{COS}}^\circ + 2g_{f,\text{O}_2}^\circ + g_{f,\text{CaCO}_3}^\circ + 2g_{f,\text{H}_2\text{O}}^\circ - 2g_{f,\text{CO}_2}^\circ - g_{f,\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}^\circ] \\ + RT \ln [(x_{\text{COS}} (x_{\text{O}_2,0})^2 / (x_{\text{CO}_2,0})^2)]$$

Why were solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and solid CaCO_3 assumed to be constituents of the stable reference environment? These assumptions were provoked by the need to find "the" stable configuration for S in our environment. It is not S itself, because S could react with O_2 from the environment to produce SO_2 and yield a net potential energy (availability) output, since ΔG for the reaction is negative. (For an exhaustive treatment of equilibrium and stability conditions, in relation to availability, see Hatsopoulos and Keenan, 1965). But neither is the SO_2 stable; it can combine with O_2 to produce SO_3 . In turn the SO_3 can react with environmental H_2O to produce H_2SO_4 , which obviously has significant potential to cause change--availability. What next? Pursuit of this question led, after extensive deliberation and study, including a search through tables of Gibbs free energies of formation (g_f° 's), to the conclusion that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was very nearly stable if not "the" stable compound containing S . In turn, unfortunately, there was a need for a stable compound of Ca , to react with S , to bring the S to stability; the search for this led

to CaCO_3 . Thankfully, this did not introduce the need for yet another compound, because reactions of S and S compounds of interest, with CaCO_3 and other environmental constituents such as O_2 and H_2O , to produce stable compounds, yield only $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CO_2 . A feature of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 which is critical to their selection as stable compounds is their abundance in our environment.

The latter completes the presentation of the theory for making thermostatic property calculations to evaluate the availability of flow streams. It should be mentioned that any kinetic energy or gravitational potential energy associated with flowing fluids has been neglected throughout; when these are not negligible it is simply a matter of adding them: $P_A = [h - T_0 s + Mv^2/2 + mgZ - \sum x_j \mu_{O_j}] I_n$.

Following is a list of convenient formulas, deduced from the above developments, for evaluating $a_{j,t}$ and $a_{j,c}$ of many of the constituents which are in gas streams of gasification systems. In particular, formulas are given for each of the constituents of Table I.

Formulas for Chemical Availability, $a_{j,c}$

$$a_{\text{CO}} = 0.59248 \ln x_{\text{CO}} + 65.788 \text{ kcal/g mole}$$

$$a_{\text{CO}_2} = 0.59248 \ln x_{\text{CO}_2} + 4.8060$$

$$a_{\text{CH}_4} = 0.59248 \ln x_{\text{CH}_4} + 198.46$$

$$a_{\text{H}_2} = 0.59248 \ln x_{\text{H}_2} + 56.235$$

$$a_{\text{H}_2\text{O}} = 0.59248 \ln x_{\text{H}_2\text{O}} + 2.0717$$

$$a_{\text{N}_2} = 0.59248 \ln x_{\text{N}_2} + 0.16518$$

$$a_{\text{H}_2\text{S}} = 0.59248 \ln x_{\text{H}_2\text{S}} + 189.94$$

$$a_{\text{COS}} = 0.59248 \ln x_{\text{COS}} + 200.61$$

$$a_{\text{O}_2} = 0.59248 \ln x_{\text{O}_2} + 0.94328$$

$$a_{\text{S}} = 139.54$$

Formulas for Thermal Availability

$$a_T = \left[\frac{A}{10^3} - \frac{T_0 B}{10^6} \right] (T - T_0) + \left[\frac{B}{2 \cdot 10^6} - \frac{T_0 C}{2 \cdot 10^9} \right] (T^2 - T_0^2) + \left[\frac{C}{3 \cdot 10^9} - \frac{T_0 D}{3 \cdot 10^{12}} \right] (T^3 - T_0^3) - \frac{D}{4 \cdot 10^{12}} (T^4 - T_0^4) - \frac{T_0 A}{10^3} \ln \frac{T}{T_0} \frac{\text{kcal}}{\text{g mole}}$$

where

	A	B	C	D
CO	6.726	.4001	1.283	-.5307
CO ₂	5.316	14.285	-8.362	1.784
CH ₄	4.750	12.0	3.03	-2.63
H ₂	6.952	-.4576	0.9563	-.2079

	A	B	C	D
H ₂ O	7.700	0.4594	2.521	-.8587
N ₂	6.524	1.448	-.2271	0.
H ₂ S	7.070	3.128	1.364	-.7867
COS	5.626	16.573	-10.868	2.499
O ₂	6.058	3.631	-1.709	.3133

For Pressure Availability

$$a_p = 0.59248 \ln \frac{P_{\text{stream}}}{P_0} \left[\frac{\text{kcal}}{\text{g mole}} \right]$$

where p is the total pressure of the flow stream.

All of the availabilities evaluated in this paper assumed a stable reference environment including, in abundance, the following components, all at

$$T_0 = 298.15^\circ\text{K} (77^\circ\text{F})$$

$$P_0 = 1 \text{ atm}$$

Components:

- Air Constituents	Mole Fraction	- Condensed phases, at T_0, P_0
N ₂	0.7567	H ₂ O
O ₂	0.2035	CaCO ₃
H ₂ O	0.0303	CaSO ₄ ·2H ₂ O
A	0.0091	
CO ₂	0.0003	
H ₂	0.0001	

Nomenclature

\dot{A} = availability per unit time
 A = availability flow per unit of coal fed to system
 a = availability (potential energy) per unit mass or per mole
 E = energy
 G = Gibbs free energy
 g = G per mole (or per unit mass)
 h = enthalpy per mole (or per unit mass)
 I = current (commodity per unit time)
 m = mass flow per unit of coal fed to system
 P = power
 p = pressure
 Q = heat (energy)
 q = change
 R = universal gas constant
 S = entropy
 s = entropy per mole (or per unit mass)
 T = temperature
 V = volume
 v = volume per mole (or per unit mass)
 v = velocity
 x = mole fraction
 Z = altitude

Greek Symbols

ϵ , effectiveness
 θ , thermal
 μ , chemical potential
 σ , surface
 ϕ , electric potential

Subscripts and superscripts

c , consumption
 c , chemical
 f , formation
 j , j th constituent
 l , loss
 n , molar
 p , production
 O , reference environment
 $^\circ$, standard state
 \cdot , time rate of change

Table II. Electrical Availability Flows

Stream No.	Use	Availability kJ/kg of coal
22	Gas Cleanup	132
23	Heat Recovery	3
24	Air Separation	9
25	Gasification	15
26	Coal Preparation	74
27	Net Electrical Output	7333

Table III. Effectiveness of Economic Sectors
and of Some Industrial Sub-sectors
(approximate, average values)Economic Sectors (Reistad, 1974):

-Production of Electricity (consumes 20% of national energy resources)	$\epsilon = 30\%$
-Residential and Commercial, Direct Consumption (15%)	$\epsilon = 10\%$
-Industrial, Direct (35%)	$\epsilon = 15\%$
-Transportation, Direct (30%)	$\epsilon = 10\%$

Industrial Sub-sectors (Gyftopoulos et al, 1975):

-Iron & Steel (15% of industrial consumption)	$\epsilon = 21\%$
-Petroleum refining (11%)	$\epsilon = 90\%$
-Pulp & Paper (5%)	$\epsilon = 10\%$ - rough estimate
-Aluminum (3%)	$\epsilon = 35\%$
-Cement, Copper, Rubber, Plastics, Glass studies are in process; detailed study has been done for iron & steel, process by process; to some degree for refining, pulp & paper, aluminum (Hall, 1975).	

Conversion Systems & Devices

-Total-Energy	
-All-electric	$\epsilon = 30\%$
-All-fossil	$\epsilon = 30\%$
-Fossil-fired power plant	$\epsilon = 35\%$
-Combustion Engines (full-load)	$\epsilon = 35\%$
-Refrigeration	$\epsilon = 40\%$
-Comfort Conditioning	
-Furnaces	$\epsilon = 10\%$
-Heat Pump	
-electricity to heat	$\epsilon = 35\%$
-overall (e.g., coal to heat)	$\epsilon = 10\%$
-electricity to cooling	$\epsilon = 5$ to 10%



WITH CHARGE, q

$$P_E = \phi I_q \quad \text{WHERE } I_q = \text{CURRENT}$$

WITH INCOMPRESSIBLE
FLUID FLOW

$$P_E = p I_v \quad \text{WHERE } I_v = \text{VOLUMETRIC FLOW RATE}$$

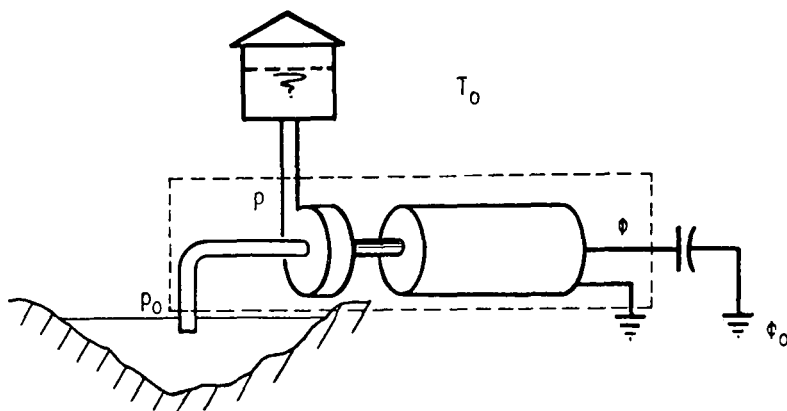
WITH CHEMICAL COMPOUND, i

$$P_E = \mu_i I_i \quad \text{WHERE } I_i = \text{MOLAR FLOW RATE}$$

WITH THERMAL CURRENT

$$P_E = T I_\theta \quad \text{WHERE } I_\theta = \text{THERMAL CURRENT}$$

FIGURE 1. TRANSPORTATION OF ENERGY THROUGH A CONDUIT VIA FLOW OF A COMMODITY



IDEAL OPERATION

$$[\phi - \phi_0] I_q \Rightarrow [p - p_0] I_v$$

REAL OPERATION

$$[\phi - \phi_0] I_q \Rightarrow [p - p_0] I_v + T_0 I_\theta$$

FIGURE 2. TRANSFER OF POTENTIAL ENERGY FROM ONE COMMODITY (CHARGE) TO ANOTHER (WATER).

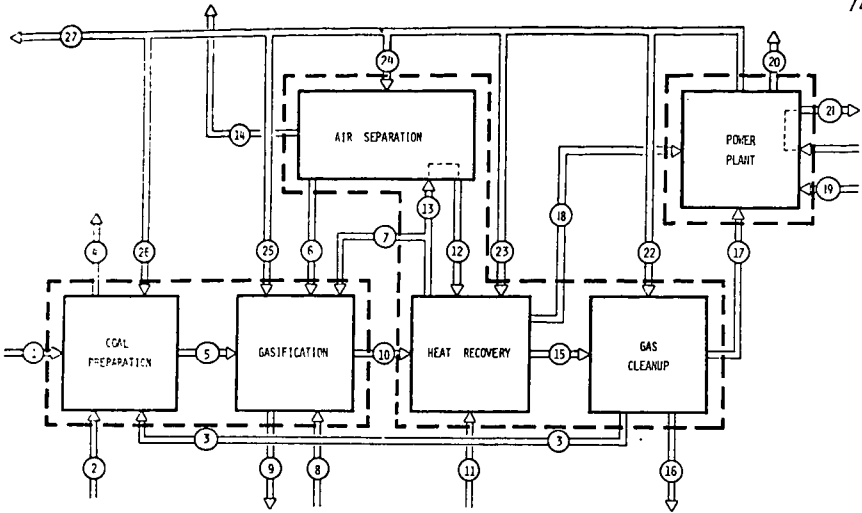


FIGURE 3 BLOCK DIAGRAM OF A TYPICAL MEDIUM-BTU GAS GENERATION AND CLEANUP SYSTEM FEEDING A CONVENTIONAL POWER PLANT

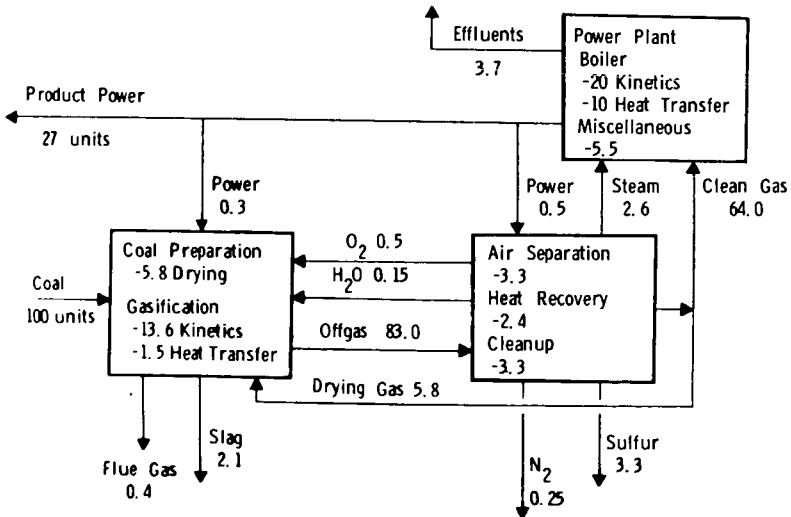


FIGURE 4. AVAILABILITY FLOW DIAGRAM FOR GASIFICATION AND POWER PLANT.

(Negative numbers represent availability consumptions.)

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